Optical Excitations in Hexagonal Nanonetwork Materials

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Abstract. Optical excitations in hexagonal nanonetwork materials, for example, Boron-Nitride (BN) sheets and nanotubes, are investigated theoretically. The bonding of BN systems is positively polarized at the B site, and is negatively polarized at the N site. There is a permanent electric dipole moment along the BN bond, whose direction is from the B site to the N site. When the exciton hopping integral is restricted to the nearest neighbors, the flat band of the exciton appears at the lowest energy. The symmetry of this exciton band is optically forbidden, indicating that the excitons relaxed to this band will show quite long lifetime which will cause strong luminescence properties.

INTRODUCTION

The hexagonal nanonetwork materials composed of atoms with ionic characters, for example, Boron-Nitride (BN) sheets and nanotubes [1], have been investigated intensively. They are intrinsically insulators with the energy gap of about 4 eV as the preceding band calculations have indicated [2,3]. The possible photogalvanic effects depending on the chiralities of BN nanotubes have been proposed by the model calculation [4]. Even though optical measurements on the BN systems have not been reported so much, it is quite interesting to predict condensed matter properties of the hexagonal nanonetwork materials.

In this paper, we investigate optical excitation properties in BN systems. The bonding is positively polarized at the B site, and is negatively polarized at the N site. There is a permanent electric dipole moment along the BN bond, whose direction is from the B site to the N site. The presence of the dipole moments will give rise to strong excitonic properties as illustrated in Fig. 1. The energy of the highest occupied atomic orbital of N is larger than that of B, and the energy of the lowest unoccupied orbital of B is smaller than that of N. Low energy optical excitations are the excitations of the electron-hole pairs between the higher occupied states of N and the lower unoccupied states of B atoms.

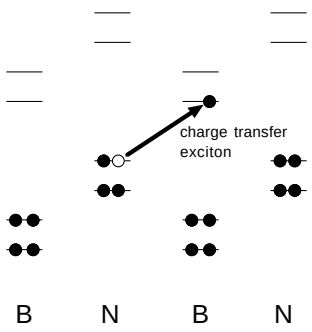

FIGURE 1. Optical excitations along the BN alternations.

EXCITONS ON THE KAGOMÉ LATTICE

We consider exciton interactions among nearest neighbor dipoles. In Fig. 2 (a), the B and N atoms are represented by full and open circles, respectively. The several arrows show the directions of dipole moments. We assume one orbital Hubbard model with the hopping integral of electrons t, the onsite repulsion U, and the energy difference Δ between the B and N sites. After second order perturbations, we obtain the following forms of the nearest neighbor interactions: $J_1 = t^2/(-\Delta + U)$ for the case of conserved excited spin (type-1 exciton) and $J_2 = t^2/\Delta + t^2/(-\Delta + U)$ for the case that spin of the excited electron flips (type-2 exciton). The condition $U > \Delta$ would be satisfied in general, and this means that J_1 and J_2 are positive. The interactions are present along the thin lines of Fig. 2 (a). After the extraction of the interactions J_1 and J_2, there remains the two-dimensional Kagomé lattice which is shown in Fig. 2 (b). Therefore, the optical excitation hamiltonian becomes:

$$\begin{aligned} H &= \sum_{\langle i,j\rangle} \sum_{\sigma=\alpha,\beta} J_1(|i,\sigma\rangle\langle j,\sigma| + \text{h.c.}) \\ &+ \sum_{\langle i,j\rangle} J_2(|i,\alpha\rangle\langle j,\beta| + |i,\beta\rangle\langle j,\alpha| + \text{h.c.}), \end{aligned} \tag{1}$$

where the indices i and j mean the vertex points of the Kagomé lattice, and the sum is taken over the nearest neighbor pairs $\langle i,j\rangle$ and the excited spin σ. The unit cell has three lattice points, namely, 1, 2, and 3, as shown in Fig. 2 (b).

The energy dispersions of the model are given in terms of wavenumbers $\boldsymbol{k} = (k_x, k_y)$:

$$E = \begin{cases} -2(J_1 + J_2), \\ (J_1 + J_2)[1 \pm \sqrt{1 + 4\cos(k_x b/2)[\cos(k_x b/2) + \cos(\sqrt{3}k_y b/2)]}], \\ 2(-J_1 + J_2), \\ (J_1 - J_2)[1 \pm \sqrt{1 + 4\cos(k_x b/2)[\cos(k_x b/2) + \cos(\sqrt{3}k_y b/2)]}], \end{cases} \tag{2}$$

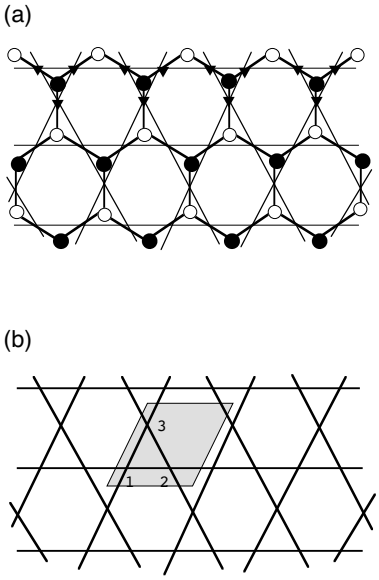

FIGURE 2. (a) The hexagonal nanonetwork of boron (full circles) and nitrogen sites (open circles). Several arrows indicate the directions of dipole moments, and the thin lines represent the conjugate Kagomé lattice network. (b) The Kagomé lattice extracted from Fig. (b). The shaded area is the unit cell, which have three lattice points indicated with numbers.

where the two dimensional x-y axes are defined as usual in Fig. 2, and $b = \sqrt{3}a$ is the unit cell length of the Kagomé lattice in Fig. 2 (b), and a is the bond length of Fig. 2 (a). There appears a dispersionless band with the lowest energy $-2(J_1+J_2)$. There is another dispersionless band at the higher energy $2(-J_1 + J_2)$. The other four bands have dispersions which are like those of the two dimensional network of electrons on the graphite. Such the appearance of the flat band has been discussed with the possibility of ferromagnetism in the literatures [5]. In the present case, the lowest optical excitation band becomes flat in the honeycomb BN plane. When the BN plane is rolled up into nanotubes, the flat band is dispersionless too. Such the flat exciton band will have strong optical density originating from the huge density of states due to the weak dispersive character.

SYMMETRIES OF EXCITON WAVEFUNCTIONS

We look at symmetries of the lowest excitons with the energy $-2(J_1 + J_2)$. The eigenvalue problem at the wavenumber $\boldsymbol{k} = (0, 0)$ gives twofold degenerate solutions $\Psi_1^\dagger = (1/\sqrt{6})(1, 1, -2)$ and $\Psi_2^\dagger = (1/\sqrt{2})(-1, 1, 0)$ both for the type-1 and type-2 exciton states. The symmetry of the solution Ψ_1 is shown in Fig. 3 (a), and that of the solution Ψ_2 is displayed in Fig. 3 (b). We find that both wavefunctions are symmetric with respect to spatial inversion, and therefore they have the symmetry

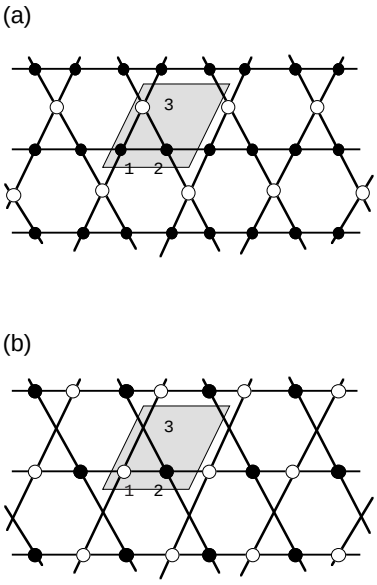

FIGURE 3. Symmetries of two wavefunctions at $E = -2(J_1 + J_2)$. The full and open circles indicate positive and negative values at the lattice point, respectively.

gerade. The transition to the lowest exciton is optically forbidden. The forbidden exciton state indicates that excitons relaxed to this lowest exciton band will show quite long lifetime which will cause strong luminescence properties. In addition, the lowest energy excitons will have huge density of state due to their flatness of the band. These properties might result in interesting optical measurements in hexagonal nanonetwork materials.

SUMMARY

The flat band of the optically forbidden exciton appears at the lowest energy in the optical excitations of BN systems. The excitons relaxed to this band might show quite long lifetime which will cause strong luminescence properties.

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